phys. stat. sol. (a) 61, K187 (1980)

Subject classification: 14.3.3; 2; 14.3.1; 22

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High Speed Memory Behavior and Reliability of an Amorphous As_2S_3 Film Doped with Ag

By

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Dedicated to Prof. Dr. Dr. h.c. Dr. E.h. P. GÖRLICH on the occasion of his 75th birthday

Introduction Concerning electrical and optical properties of amorphous semiconductors, there have been many reports published and some of them were on electrical switching /1, 2/.

Switch and memory phenomena in amorphous materials so far are mainly caused by such structure change as amorphous to crystalline or vice versa /1/. However, we found that an amorphous As_2Se_3 sample with photo-doped Ag shows a non-volatile memory effect, and reported the electrical characteristics and temperature dependence of the sample, revealing that the switch and memory mechanism is strongly related to the behavior of Ag atoms diffused in the amorphous As_2Se_3 /3/. This means that switch and memory effects of the present device are essentially different from the widely known switch and memory effects of the amorphous semiconductors where the phase transition is thought to be responsible.

In this paper, we describe experimental results of high speed memory performance due to the new mechanism, and the electrical reliability and persistency of the present sample. A memory phenomenon in some nanoseconds is observed though the migration of Ag atoms may be concerned. In this switching the device has no (so called) prememory time in the process between a switching and a memory state. Therefore it will be expected that improving the device structure brings forth more rapid memory performance.

Sample preparation A sample structure is shown in Fig. 1. The preparation method of the sample is as follows: (i) A bottom electrode 4 cm^2 wide of Mo is

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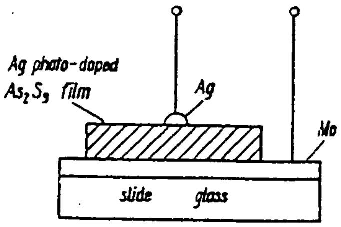

Fig. 1. Schematic illustration of a As_2S_3 memory device

made by rf sputtering on a glass slide; (ii) the amorphous As_2S_3, which is prepared in advance by a conventional preparation method, is evaporated in a pressure less than 10^{-5} Torr on to the bottom electrode. The growth rate of the As_2S_3 film is estimated less than 30 Å/s and the final thickness is about 1 μm; (iii) Ag metal is evaporated on the As_2S_3 film upto 200 to 500 Å thickness; (iv) then, the metallic Ag thus evaporated is irradiated by a mercury lamp to diffuse into the amorphous As_2S_3 film. This is known as a photo-doping /4, 5/ of Ag and believed essential in the preparation of the present sample. Disappearance of the metallic reflection of Ag on the film surface is used for a criterion of the end of photo-doping; (v) finally, a dip of Ag paste is attached to the film as a top electrode whose area is about 2 mm^2. The present sample is a diode of Ag-As_2S_3-Mo structure.

Experimental results and discussion Fig. 2 illustrates photographs of typical device responses (2) to the applied repetitive rectangular pulses (1) of 100 kHz. Fig. 2a gives a memory write time in which OFF to ON transition occurs (the arrows indicates the process of switch and memory). The OFF state resistance for the present sample seems to range from 10^4 to 10^5 Ω while the ON state one from 10 to 10^2 Ω. The response wave-form implies: (i) The memory write time is less than 10 ns. (ii) A time for fastening memory is not observed though conventional amorphous semiconductor memory devices have been reported to have some delay time for fastening the memory. Then, the present device seems to perform switching and memorizing operations simultaneously. (iii) The memory is non-volatile in operation. Fig. 2b shows a memory erase time in which ON to OFF tran-

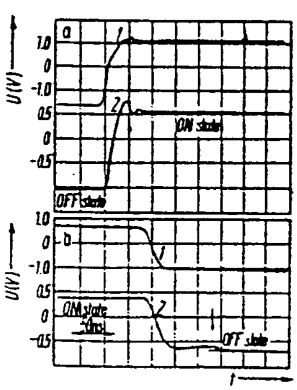

Fig. 2. Typical device responses to the applied repetitive rectangular pulses. a) OFF to ON transition (memory write time). b) ON to OFF transition (memory erase time) ((1) applied voltage pulse, (2) device response)

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(i) The memory erase time
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optical microscopic observation.
dendrite) in the As_2S_3 film bridg
ory phenomenon /3/. However
ionic process under existence of
ionic) migration in the present r
speed memory time such as nano
electronic processes should exis
In an application of memory
write and erase cycle times, the
temperature range, and persiste
Table 1.

It was confirmed that the pre
temperature range from room te
was not broken at such an elevat

Table 1

Reliability test results

operating temperature (upper limit)
storage temperature (upper limit)
memory write and eras
persistency

sition occurs (the arrow indicates the process of switch and memory). The device response waveform implies:

(i) The memory erase time is 20 ns approximately and larger than the memory write time in value. (ii) A delay time exists in the memory erase process.

From the above mentioned results, it is considered that the memory phenomenon for the present sample is caused not by the phase transition between amorphous state and crystalline state but by the other mechanisms. In fact, optical microscopic observations clarified that whisker-like metallic Ag (Ag dendrite) in the As_2S_3 film bridges between electrodes and brings forth the memory phenomenon /3/. However, the bridge formation may result from some ionic process under existence of an electric field, the velocity of Ag atomic (or ionic) migration in the present media could not be so rapid to explain the high speed memory time such as nanoseconds. So that, it is believed that some electronic processes should exist in addition to the ionic process.

In an application of memory device, it is necessary to check the memory write and erase cycle times, the maximum operating temperature, the storage temperature range, and persistency /6/. Test results are summarized in Table 1.

It was confirmed that the present device shows memory performance in the temperature range from room temperature to 150 °C and at storage, the device was not broken at such an elevated temperature as 180 °C.

Table 1

Reliability test results

operating temperature (upper limit)	150 °C
storage temperature (upper limit)	180 °C
memory write and erase cycle	$> 10^8$
persistency	> 3 years

This is better performance than Ge devices and is comparable to Si devices. Memory write and erase cycle times of 10^8 have been obtained at present, and the test are now being continued. The persistency of the sample is over three years and is under test now too.

Conclusion From the above mentioned experimental results, it was concluded that the present device is excellent at both thermal characteristics and durability. Although the switch and memory transition time is about 10 ns, it will be possible to reduce the transition time upto picosecond order by decreasing the capacitance of device.

The authors would like to acknowledge sample preparations and measurements by Y. Toyoda.

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(Received July 17, 1980)

phys. stat. sol. (a) 61,

Subject classification: 20

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Evidence for Optical Abs

By

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Dedicated to Prof. Dr. D
on the occasion of his 75

Introduction In more recent opt
Blazey /2/, in agreement with e
5/, attributed absorption bands
reduced samples to components
Fe^{2+} in octahedral sites. Howev
specimens containing concentrat
sorption in the near infrared (NI
to arise from an underlying band
was alternatively assigned by Bl
(in /1/) to $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+}$
made to detail more clearly the
time to confirm or deny previous
than one band may be involved) a
to 13000 ppm Fe have been heat
sured at room temperature and he
results obtained with data from
that it is Fe^{2+}-Fe^{3+} interactions,
important role in assigning featu
moderate iron concentrations.

Experimental The two batch
vestigated were obtained from W
12800 ppm by weight of Fe accor

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